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The Patent Office

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1. Your reference

SCE/GH/DBN.104

2. **9914879.3** 26 JUN 1999

3. Full name, address and postcode of the or of each applicant *(underline all surnames)*

Trikon Holdings Limited,
Coed Rhedyn,
Ringland Way,
Newport,
Gwent,
NP6 2TA

Patents ADP number *(if you know it)*

7435423001

If the applicant is a corporate body, give the country/state of its incorporation

United Kingdom

4. Title of the invention

Method and Apparatus for forming a Film on a Substrate

5. Name of your agent *(if you have one)*

"Address for service" in the United Kingdom to which all correspondence should be sent *(including the postcode)*

Wynne-Jones, Laine & James,
Essex Place,
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Gloucestershire,
GL50 1JJ
United Kingdom

Patents ADP number *(if you know it)*

1792001

6. If you are declaring priority from one or more earlier patent applications, give the country and the date of filing of the or of each of these earlier applications and *(if you know it)* the or each application number

Country	Priority application number *(if you know it)*	Date of filing *(day / month / year)*

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Number of earlier application	Date of filing *(day / month / year)*

8. Is a statement of inventorship and of right to grant of a patent required in support of this request? *(Answer 'Yes' if:*
a) any applicant named in part 3 is not an inventor, or
b) there is an inventor who is not named as an applicant, or
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Continuation sheets of this form	
Description	8
Claim(s)	3
Abstract	
Drawing(s)	3

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Priority documents	
Translations of priority documents	
Statement of inventorship and right to grant of a patent *(Patents Form 7/77)*	
Request for preliminary examination and search *(Patents Form 9/77)*	1
Request for substantive examination *(Patents Form 10/77)*	
Any other documents *(please specify)*	

11. I/We request the grant of a patent on the basis of this application.

Signature Wynne - Jones, Laine & James Date 25.6.99

Wynne-Jones, Laine & James

12. Name and daytime telephone number of person to contact in the United Kingdom — Mr. S.C. Eastwood (01242) 515807

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Method and Apparatus for forming a Film on a Substrate

This invention relates to a method and apparatus for forming a film on a substrate particularly, although not exclusively, to a film which is deposited on a semiconductor silicon wafer with flowing properties and retains carbon-containing groups on annealing.

A number of methods have been disclosed for depositing a thin film on a semiconductor wafer, and examples include US 5314724, US 4892753, US 5593741, EP-A-0731982 and EP-A-0726599. It can be seen from these that, up until recently, organic containing silicon precursors have been processed or further processed in such a way as to avoid or subsequently remove organic components from the as-deposited film; this is, for example, disclosed in US 5314724. In addition, it has been found to be difficult to retain both good film quality and good gap-fill capability on the surfaces and in recesses of a wafer on which the film is deposited.

According to a first aspect of the present invention, there is provided a method of forming a film on a substrate comprising:

(a) positioning the substrate on a support in a chamber;

(b) supplying to the chamber in gaseous or vapour form a silicon-containing organic compound and an oxidising agent in the presence of a plasma to deposit a film on the substrate; and

(c) setting the film such that carbon-containing groups are retained therein.

Thus, the present invention provides a method of

forming a film in which a flowing intermediate film is achievable, thus providing good gap fill properties on the substrate.

The substrate may be a semiconductor wafer, for example a silicon semiconductor wafer of the type known in the art.

Preferably, the oxidising agent is oxygen, although others could be used, for example H_2O_2.

For example, the silicon-containing organic compound may be an organosilane or an organosiloxane. Preferably, the silicon-containing organic compound is an alkylsilane, and even more preferably is a tetraalkysilane. In a particularly preferred embodiment of the invention, the silicon-containing organic compound is tetramethylsilane (TMS). However, for example, other organosilanes or organosiloxanes could be used, one example being 1,1,3,3-tetramethyldisiloxane (TMDS).

The film may be deposited on a substrate positioned on a low-temperature support, for example a support at a temperature of about 0°C.

In one embodiment, the method may further comprise supplying RF power during deposition of the film. This RF power is preferably applied to a showerhead or the like through which the gaseous precursors are passed into the chamber.

Whilst any suitable experimental conditions may be used, it has been found that typical conditions include a flow rate of 210 sccm tetramethylsilane, a flow rate of 200 sccm O_2, a chamber pressure of 2000 mT, a support temperature

of 0°C and a showerhead temperature of 100°C, and 250 watts of 380 khz RF power applied to the showerhead, although it is pointed out that these are only typical conditions.

The setting of the film may be carried out by an annealing step, for example at a temperature of about 450°C which serves to remove water from the deposited film. It has been found that a typical k value of the set film is about 2.55, for example for a 6000Å thick film deposited without a base layer (prior to deposition of the film) or capping layer (on the formed layer) after an annealing step at about 450°C in the absence of oxygen. This k value is a measure of the dielectric constant and it can be seen that the present invention provides a particularly low dielectric constant.

According to a second aspect of the present invention, there is provided a method of forming a film on a substrate comprising:

(a) positioning the substrate on a support in a chamber;

(b) supplying to the chamber in gaseous or vapour form tetramethylsilane and oxygen in the presence of a plasma and a supply of RF power to deposit a film on the substrate; and

(c) setting the film such that carbon-containing groups are retained therein.

According to a further aspect of the present invention, there is provided an apparatus for forming a film on a substrate, the apparatus comprising:

(a) a support for the substrate positioned in a chamber;

(b) means for supplying to the chamber in gaseous or vapour form a silicon-containing organic compound and an oxidising agent in the presence of a plasma to deposit a film on the substrate; and

(c) means for setting the film such that carbon-containing groups are retained therein.

The apparatus may, in one embodiment, further comprise means for improving the uniformity of the deposition of the film on the substrate. This may be arranged in the region of, or around, a showerhead and, whilst the applicant is not to be restricted hereby, it is thought that its role in the uniformity of deposition is possibly as a result of providing a site for surface reactions about the surface periphery thus enhancing deposition rate at the edge of the substrate.

Although the invention has been defined above, it is to be understood that it includes any inventive combination of the features set out above or in the following description.

The invention may be performed in various ways and a specific embodiment will now be described, by way of example, with reference to the accompanying drawings, and in which:

Figure 1 is a schematic view of an apparatus for use in the present invention;

Figure 2 is a Fourier Transform infrared (FTIR) spectrum showing an as-deposited and annealed film according to this invention; and

Figures 3(a) and 3(b) are scanning electron micrographs

showing the annealed film formed by the present invention.

Referring to Figure 1, there is shown an apparatus generally at 1 which includes a vacuum chamber 2 having a showerhead 3 and a wafer support or platen 4. The showerhead 3 is connected to an RF source (not shown) to form one electrode, whilst the support 4 may be earthed to form another electrode. Alternatively, the RF source could be connected to the support 4 and the showerhead 3 earthed. The showerhead 3 is connected via pipes (not shown) to respective sources of tetramethylsilane and oxygen. The apparatus is generally of the form disclosed in EP-A-0731982, which is incorporated herein by reference. However, a standard (non-duplex) showerhead is normally used. Also shown is a uniformity ring 5 arranged around the showerhead 3. This ring 5 plays an active role in the uniformity of deposition of the film on the wafer.

In use, the apparatus 1 is arranged to deposit a flowable intermediate layer on a wafer to produce planarisation or for "gap filling". The film is formed by introducing into the chamber tetramethylsilane and oxygen in gaseous or vapour form and reacting them within the chamber. This forms a flowing intermediate layer even when a plasma is present. It has been found that very small dimensioned gaps can be filled by the process of the present invention. The reaction takes place in the presence of a plasma. Subsequently, the film is annealed by heating, preferably in the absence of oxygen.

Example

The precursor tetramethylsilane (TMS) has been applied with various other precursors, a platen temperature of approximately 0°C and RF power where indicated. The basic results were as follows:

TMS + H_2O_2	No deposition in the pressure range up to 5,000mT
TMS + $MeSiH_3$ + H_2O_2	Slight increase in carbon content over just $MeSiH_3$ + H_2O_2. Deposition rate ~6000 Å/min
TMS + SiH_4 + H_2O_2	No carbon in the film. Deposition rate ~9000 Å/min
TMS + H_2O_2 + RF	Deposition rate ~4000 Å/min. High refractive index
TMS + O_2 + RF	Deposition rate over 2 micron/min -high carbon content.

A 'preferred' process was then developed consisting of:

210sccm TMS (calculated from fill rate checks)

200sccm O_2

2,000 mT pressure

0° platen temperature and 100°C showerhead temperature

250 watts if 380khz RF power applied to the showerhead.

This yielded a k value of 2.55 (measured by CV techniques) for a 6,000Å thick film deposited without base or capping layer after an anneal at approximately 450°C in the absence of oxygen.

Figure 2 shows a FTIR spectrum for an as-deposited and annealed film according to this invention. The two spectra

are shown overlain on the same diagram for ease of comparison. The as-deposited spectrum is the lower of the two and shows at 6 the characteristic peak of O-H bonds associated with water. Between 3,600 and 3,000 wave numbers O-H bonds associated with free water, isolated O-H and H bonded O-H are present. Water contains free water and H bonded O-H and thus gives a characteristically broad peak in this area. At 7 is the $C-H_3$ peak; at 8 is the $Si-CH_3$ peak (Si-C); and at 9 is the Si-O peak.

It can thus be seen that a film has been deposited containing water which is subsequently removed by the annealing step and that CH_3 is present, is bonded to Si and remains in the film after annealing to form the hard film.

Generally, an indicator of low k characteristics is a high Peak Area Ratio (PAR) between Si-C and Si-O on the FTIR. It is believed Si-C bonds block Si-O bonds and thus reduce the density of the resultant film. Hence, a high Peak Area Ratio Si-C:Si-O is indicative of a low k film. It was however noted that for these plasma deposited films the measured k values were not as low as the Peak Area Ratio Si-C:Si-O would suggest from non plasma deposited low k films deposited from a reaction of methylsilane and peroxide.

Films of this invention as annealed are shown in Figure 3 which demonstrate the flowing characteristics of the as-deposited film.

In general, the following effects of changing the parameters in a process have been observed:

Parameter	Property			
	Refractive Index	FTIR Peak Area Ratio SiC/SiO	CH/SiO	Uniformity
Pressure Increase	down	up	up	better
Power increase	none	down	down	better
Nitrogen flow increase	up	down	down	worse
TMS/O_2 ratio increase	down	up	up	none
Total TMS/O_2 decrease	none	down	down	none

CLAIMS

1. A method of forming a film on a substrate comprising:
   (a) positioning the substrate on a support in a chamber;
   (b) supplying to the chamber in gaseous or vapour form a silicon-containing organic compound and an oxidising agent in the presence of a plasma to deposit a film on the substrate; and
   (c) setting the film such that carbon-containing groups are retained therein.

2. A method according to claim 1, wherein the oxidising agent is oxygen.

3. A method according to Claim 1 or 2, wherein the silicon-containing organic compound is an alkylsilane.

4. A method according to any preceding claim, wherein the silicon-containing organic compound is a tetraalkylsilane.

5. A method according to Claim 4, wherein the silicon-containing organic compound is tetramethylsilane.

6. A method according to any preceding claim, wherein the film is deposited on a substrate positioned on a low temperature support.

7. A method according to Claim 6, wherein the support is at a temperature of about 0°C.

8. A method according to any preceding claim, further comprising supplying RF power during deposition of the film.

9. A method according to any preceding claim, wherein the set film has a k value of about 2.55.

10. A method of forming a film on a substrate comprising:

(a) positioning the substrate on a support in a chamber;

(b) supplying to the chamber in gaseous or vapour form tetramethylsilane and oxygen in the presence of a plasma and a supply of RF power to deposit a film on the substrate; and

(c) setting the film such that carbon-containing groups are retained therein.

11. A method substantially as hereinbefore described with reference to the accompanying drawings and examples.

12. An apparatus for forming a film on a substrate, the apparatus comprising:

(a) a support for the substrate positioned in a chamber;

(b) means for supplying to the chamber in gaseous or vapour form a silicon-containing organic compound and an oxidising agent in the presence of a plasma to deposit a film on the substrate; and

(c) means for setting the film such that carbon-containing groups are retained therein.

13. An apparatus according to Claim 12, further comprising means for improving the uniformity of the deposition of the film on the substrate.

14. An apparatus according to Claim 13, wherein the means for improving the uniformity is arranged around a showerhead.

15. An apparatus substantially as hereinbefore described with reference to, and as illustrated in, the accompanying

drawings.

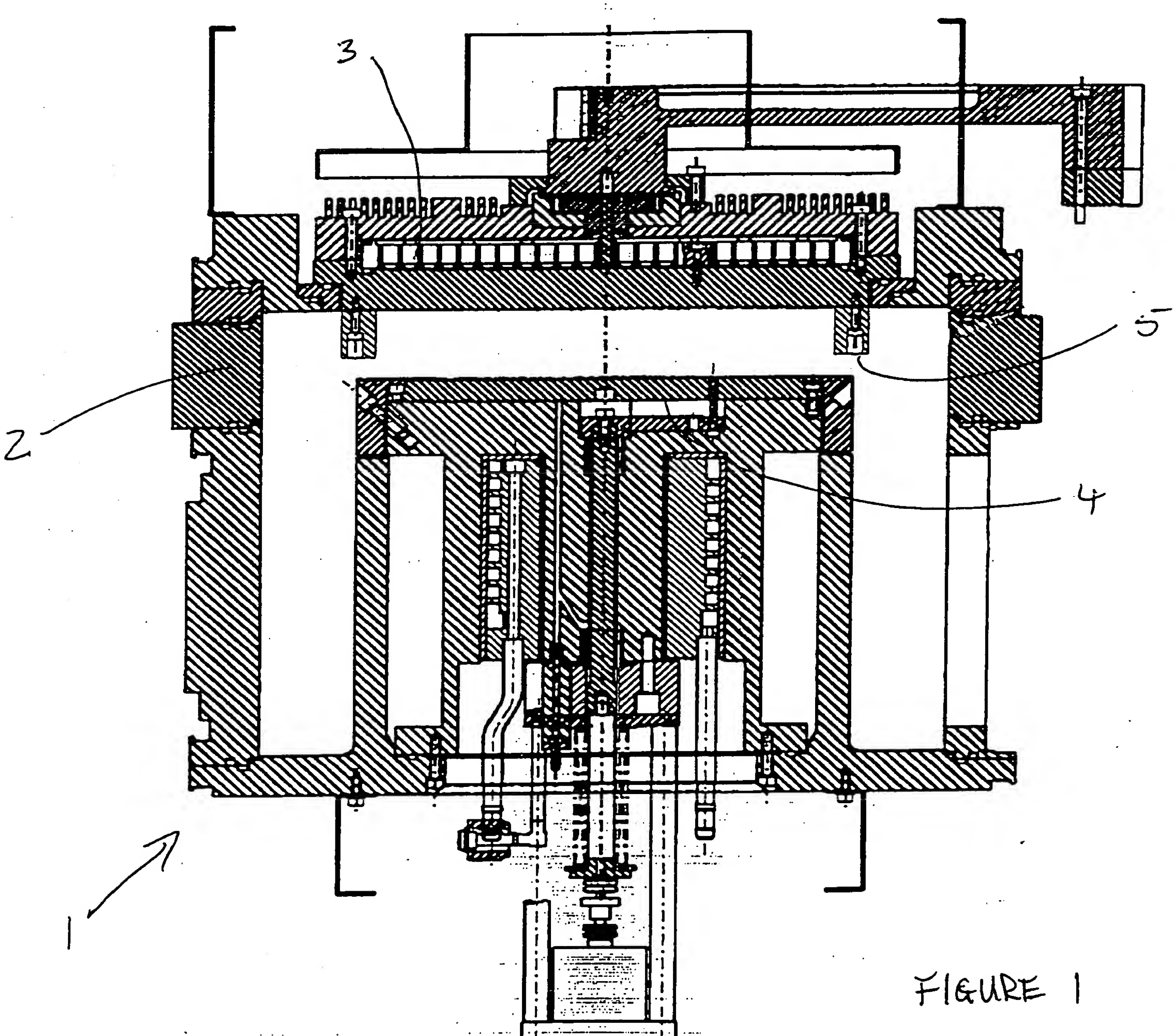
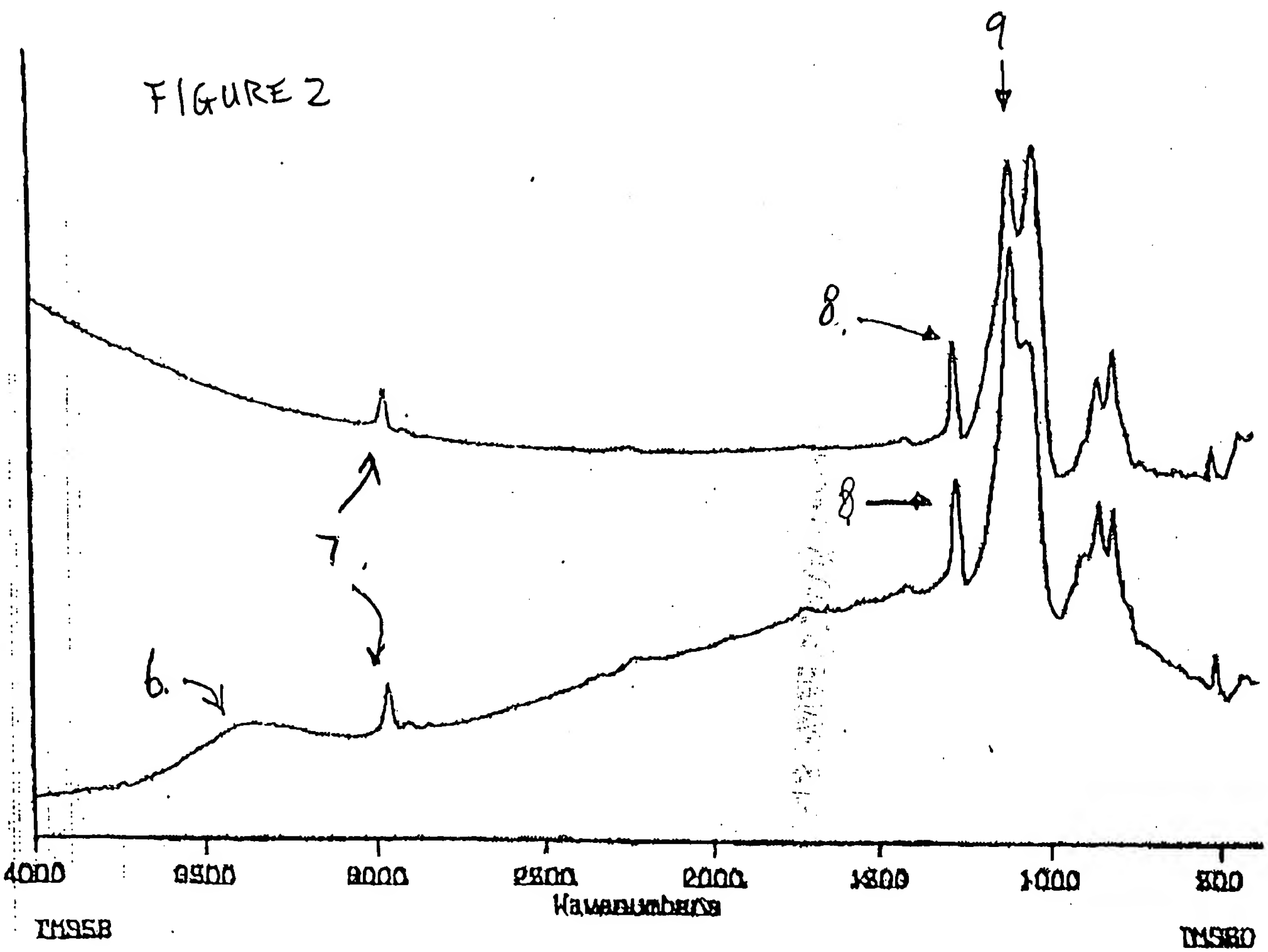
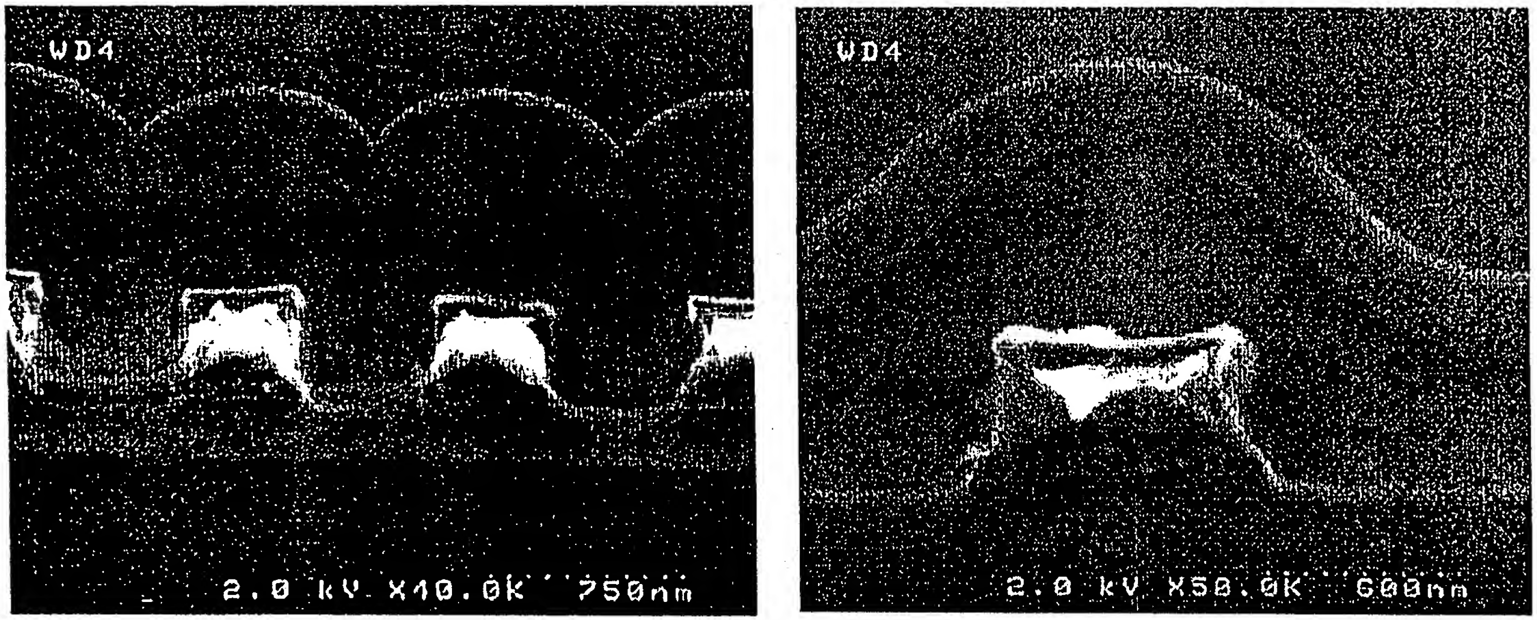


FIGURE 1

FIGURE 2



210/200 TMS/O_2 2000 MT 250 W 0°C PLATEN PRE AND POST ANNEAL



(a) (b)

FIGURE 3

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Wynne Jones Laine & James

6 July 2000